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THERMOLUMINESCENCE ANALYSIS OF RAW AND CERAMIC MATERIALS

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A method for analysis of silicate materials based on excitation of the materials with x-ray radiation and subsequent recording of thermally stimulated luminescence is considered. The possibility of analyzing the structure of raw materials and ceramics using the method proposed is displayed.

One of the areas of research and improvement of the production of the raw materials and ceramic products is the application of non-traditional investigation methods, such as thermoluminescence analysis, in addition to the traditional ones (DTA, radiography etc.) [1]. The method of thermally stimulated luminescence (TSL), in contrast to the traditional ones, makes it possible to perform fast analysis of physico-chemical processes in different stages of ceramic production including the sintering stage.

In the present experiment, the sintering of diopside ceramics of different compositions was tested by the traditional methods and by measuring TSL in the samples excited by x-rays.

The raw material and ceramic samples were excited by x-rays emitted by a BSV-2 (Mo) tube with voltage of 50 kV and current of 20 mA. The distance from the tube focus to the sample was 6 cm. The excitation duration varied from 1 to 300 min. After exposure, the samples were heated in air at the rate of 8 K/min. The temperature of the samples within the range of 300–600 K was measured with a chromel-alumel thermocouple. The integral luminescence was registered with a FEU-39A photoelectronic multiplier, and the data from the instruments were recorded with a two-coordinate potentiometer.

The materials, mixtures and diopside and steatite ceramic samples were prepared in accordance with standard sintering technology [2]. Firing was carried out in an electric furnace with Silit heaters.

One of the basic objects of investigation was diopside S-19 from Slyudyanskii deposit in the Irkutsk Region (diopside 95%, calcite 3.6%, quartz 0.7%, impurity oxides TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , Na_2O , K_2O , P_2O_5 comprise in sum 0.7%). Visually and seen with a microscope, diopsidite is a bright white powder with particles sizes from fractions of a

micrometer to 300 μm and more. The crystals have an elongated shape with clearly visible cleavage planes.

Along with transparent crystals, some low-transparency crystals are found. The x-ray phase analysis of the initial S-19 powder reveals x-ray reflections typical of diopside.

Diopside is colorless and transparent or white and semi-transparent, in mass it is white and forms crystals of prismatic and thick-tablet habit. The size of the crystals varies from 0.05 mm to 1 mm and more. The stoichiometric composition of diopside is almost perfect. The optical and x-ray diffraction parameters of the crystal are practically identical to the standard parameters for pure diopside. The tremolite (3–4%) that forms part of the diopsidite is represented by a purely magnesian variety with a minimum share of structural impurities. The calcite has a low magnesian content (0.1–0.2% MgO), and the content of iron and manganese in it does not exceed fractions of a per cent.

DTA of the diopside reveals the presence of a single endothermic effect around 1170 K related to decarbonization of the calcite [4]. In order to carry out x-ray phase analysis of diopsidite C-19, heat treatment was applied first to the initial material and then to the material after removal of calcite (treatment with hydrochloric acid). The initial material and the products after treatment were fired at the temperatures of 1073, 1173, 1273, 1373, 1473, 1523, and 1570 K (the heating time at the temperatures specified was 30 min). The x-ray phase analysis of the products of heat treatment established that in the initial material the basic x-ray reflection $d = 3.24 \text{ \AA}$ is maintained. At 1473 K, the second line intensity ($d = 3.00 \text{ \AA}$) is equal to 75% of the first line. At 1573 K both lines have approximately equal intensities but the line $d = 2.56 \text{ \AA}$ becomes the main one, and at 1573 K $d = 2.014 \text{ \AA}$. Crystal phases forming at a temperature equal to or above 1523 K were not found.

The conversion of natural diopside to the heat treatment product with $d = 3.00 \text{ \AA}$ in the initial sample proceeds am-

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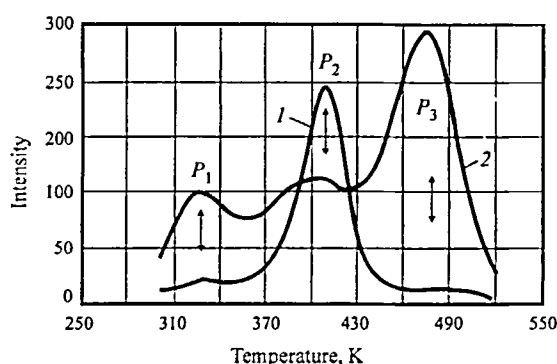


Fig. 1. Dependences of the intensity of TSP of S-19 material on the temperature: 1) initial sample; 2) same sample after firing at 1523 K (radiation time 5 min).

biguously and not to the end. In the sample without calcite, this conversion occurs without difficulty in the temperature range of 1173–1473 K, and the structure of the diopside subjected to heat treatment is maintained up to 1573 K. At 1573 K, the x-ray reflections do not correspond to the structure (the maximum at $d = 1.4 - 1.5 \text{ \AA}$). The powder particles melt and react with the material of the corundum crucible.

Therefore, in heat treatment of diopsidite of the composition listed above, two polytypes are revealed: the first is the natural type with $d = 3.23 - 3.24 \text{ \AA}$, and the second is diopside obtained on firing with a main line $d = 3.00 \text{ \AA}$. Both polytypes are preserved up to firing temperatures of 1473–1523 K, and the transition of the first polytype into the second one depends to a great extent on the presence of impurity minerals in the material. [5]. This process is unambiguously recorded in the analysis of this material with TSL method.

As can be seen from Fig. 1, the initial diopsidite exhibits TSL peaks with their maximums at 331 K (P_1), 423 K (P_2), and 486 K (P_3). After firing, the intensity of peaks P_1 and P_3 increase significantly without changing their position on the temperature scale. The intensity of peak P_2 after firing decreases almost by half, and its maximum on the temperature scale is shifted to 416 K. These results correlate with the changes in the intensity of the main lines of diopsidite x-ray reflections mentioned above [5].

The intensity of the different TSL peaks increases as the radiation period increases, and eventually reaches the saturation level. After that, their slow decline is observed (Fig. 2). This nature of the kinetic curves shows that it is advisable to select the radiation duration at the stage of the increase in the TSL peak intensity (in the interval of 5–30 min) since a further increase in the radiation dose does not increase the sensitivity of the method.

The radiation dose in the exposure range specified did not affect either the spectral composition or the temperature position of the TSL peaks.

The TSL curves of diopside ceramics of different compositions contain 3 peaks, the same as in the case of the initial powder. The temperature position T_p of the TSL peak maxi-

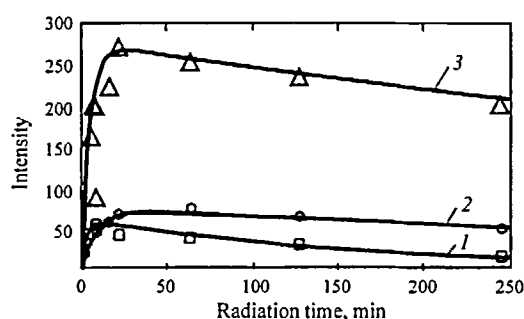


Fig. 2. Dependences of the TSL peak intensity of ceramics DK-35 on the radiation dose: 1) P_1 ; 2) P_2 ; 3) P_3 .

mums and the intensity I_p of the peaks for a radiation time of 30 min are given in Table 1.

In the discussion of the experimental results, we followed the assumption of the recombination luminescence zonal model according to which, all other terms being equal, the position of the TSL peaks is determined by the energy depth of the capture centers (traps) of the charge carriers taking part in recombination [6]. According to this assumption, three groups of charge carrier traps of different depth can be distinguished in the initial S-19 material, and their emptying determines the respective TSL peaks. Firing of the S-19 material at 1573 K practically does not affect the trap depth of groups P_1 and P_3 and slightly decreases the depth of the traps of group P_2 . The thermal stability of the trap energy spectrum shows that heat treatment of diopside does not result in alteration of the short-range order determining the trap depth. On the other hand, the changes in the relationship between the TSL peak intensities point to a change in the concentration of the traps whose emptying on heating is responsible for these TSL peaks.

It can be assumed that the traps and, particularly the traps of groups P_1 and P_3 , whose concentration increases sharply after firing are determined by the inherent thermal defects of the crystal lattice of the diopside.

On the example of ceramics of different chemical compositions, one can observe the effect of the possible modification of diopside on the trap parameters.

It seems likely that in the process of sintering of the ceramics, the reconstruction of diopside takes place accompanied by introduction of isomorphous impurities. A more radical change in the stoichiometric composition is also possible,

TABLE 1

Material	T_1, K	I_1	T_2, K	I_2	T_3, K	I_3
S-19:						
before annealing	331	9	423	78	486	5
after annealing	331	4	416	4.5	486	96
DK-37	306	80	416	480	486	920
DK-39	306	80	416	370	486	1000
DK-35	318	200	416	340	486	1330
DK-33	318	250	416	820	486	3000

TABLE 2

Material	Content, wt. %					Content of vitreous phase in ceramics*, %
	SiO ₂	BaO	Al ₂ O ₃	Fe ₂ O ₃	R ₂ O	
DK-37	50.02	44.60	4.21	0.62	0.55	27.43
DK-39	53.01	41.16	4.82	0.36	0.65	30.24
DK-35	57.14	37.27	4.33	0.66	0.60	24.61
DK-33	60.30	32.42	6.10	0.41	0.77	28.20

* Annealing temperature of sintered (water absorption 0.02%) ceramics is 1443 – 1463 K. According to the x-ray phase analysis data, the crystalline phase (diopside) has the maximum intensity line at $d = 3.00$ Å.

including the formation of new crystal phases (polytypy). We call it the thermochemical modification (TCM) of diopside.

As the result of TCM, an evident decline of the P_2 and P_3 temperature maximums of TSL peaks is observed, equal in magnitude for all types of ceramics independently of the vitreous phase composition. This is evidence of the fact that the traps responsible for these TSL peaks are most probably related to the inherent defects of the diopside, and the change in the trap energy is determined by a certain change in the short-range order caused by deviation from the stoichiometric composition of the diopside (e.g., as a result of the change in the relative concentration of SiO₂).

As for the low-temperature peak P_1 , the change of its temperature position T_1 proved to be dependent on the chemical composition of the vitreous phase of the ceramics. The most significant decrease in T_1 was observed in materials DK-37 and DK-39. Next materials DK-33 and DK-35 can

be distinguished. Table 2 gives the rated chemical composition of the ceramic vitreous phase. It is seen that the intensity of the TSL peaks increases proportionately to the increase in the content of silicon oxide in the vitreous phase with a decrease in barium oxide and a nearly equal amount of aluminum oxide, iron, and alkali metals.

The dependence of the value T_1 on the composition of the vitreous phase makes it possible to use this parameter for identifying the types of ceramics. For the same purpose, the relationship between the intensities of TSL peaks can be used (Table 1). The interrelation between the composition of the vitreous phase and the intensity of the high-temperature peak P_3 is especially evident.

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